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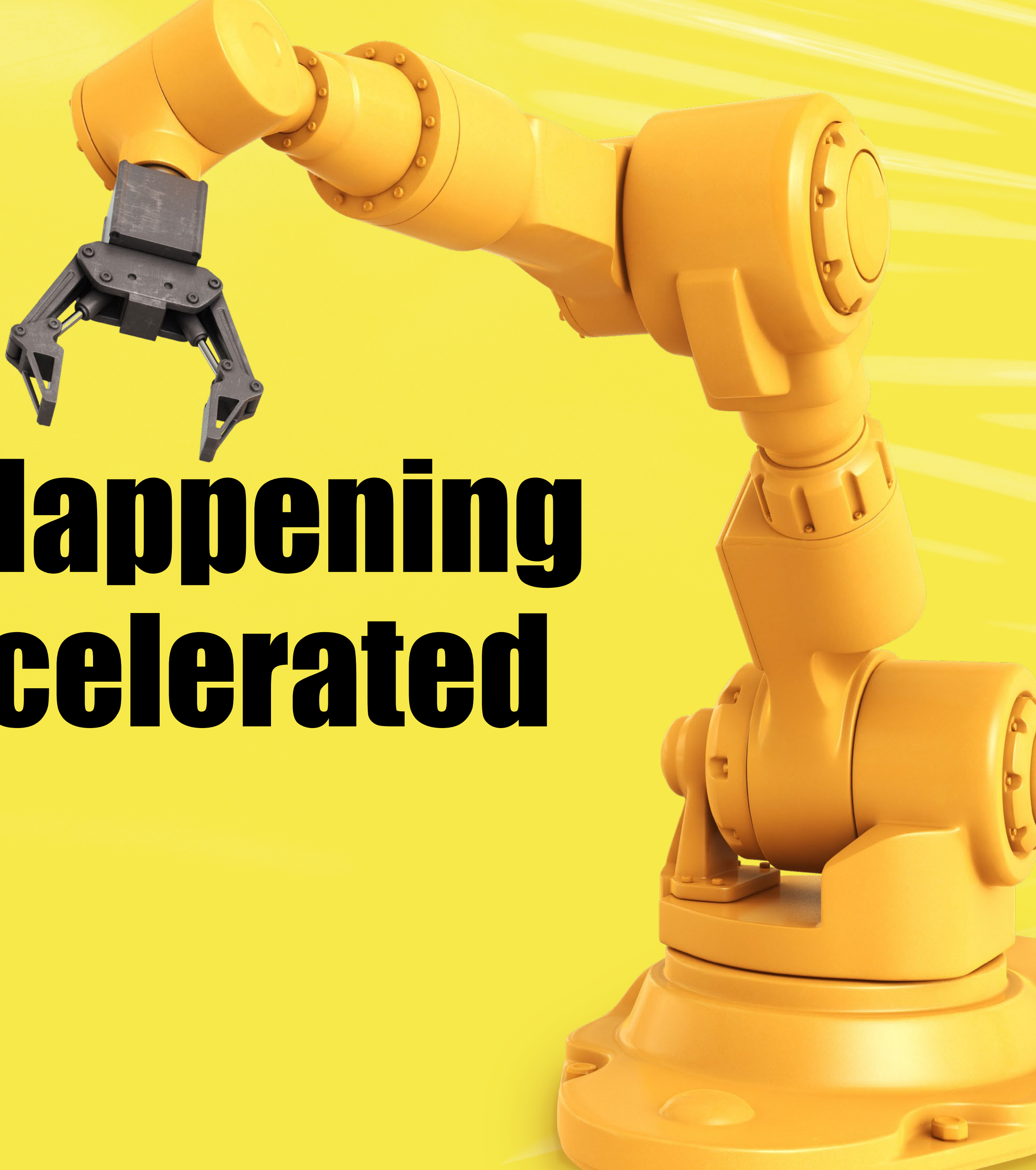

What's Really Happening During Your Accelerated Aging Tests

May 8, 2024

Jeff is a proven plastic professional with more than 30 years of experience and has performed over 5,000 investigations. He specializes in failure analysis, material selection, as well as compatibility, aging, and lifetime prediction studies for thermoplastic materials. Jeff presents webinars and seminars, covering a wide range of topics related to plastics failure, material performance, testing, and polymer technology. Jeff is a Fellow of the Society - the Society of Plastics Engineers.

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Goals

Today's talk….

- Gain an appreciation of the underlying principles behind accelerated aging of plastics.
- Understanding that the accelerated aging of plastics can be complicated by the simultaneous action of multiple mechanisms.

Agenda

Today's talk….

- Lifetime Prediction Overview
- Accelerated Thermal Aging
- Alternate Mechanisms
- Relative Thermal Index

Lifetime Prediction

Lifetime Prediction

Field Factors

Once the formed part is installed in service, the performance / lifetime is determined by:

- Stress
  - Mechanical
  - Electrical
- Temperature
- Exposure
  - Chemicals
  - Radiation

Lifetime Prediction

Agent	Type of Aging or Effect
Heat / Temperature	Thermo-oxidation, Crosslinking, Reversion, Physical Properties, Expansion/Contraction
Light	Photo-oxidation, Weathering
Ionizing Radiation	Radio-oxidation, Crosslinking
Humidity	Chemical Degradation, Hydrolysis, Swelling, Diffusion, Additive Extraction, Softening
Chemical Agents	
Mechanical Stress	Overload, Fatigue, Creep, Set, Wear
Electrical Stress	Electrical Breakdown

Lifetime Prediction

Approaches

- Experience
- Real and Simulated Service Trials
- ***Accelerated Testing***

Lifetime Prediction

Accelerated Testing

- Creep
- Fatigue
- Environmental Stress Cracking
- Molecular Degradation
  - ***Thermo-oxidation***
  - UV Radiation / Photo-oxidation
  - Chemical Attack

Lifetime Prediction

Key Question: What happens in service?

- Are there single or multiple mechanisms at work on the part while in service?
- If multiple mechanisms are present, do they act on the part simultaneously or sequentially?
- Do the mechanisms result in an immediate gradual response, or is there a long initiation period followed by sudden property loss and failure

Accelerated Thermal Aging

Accelerated Thermal Aging

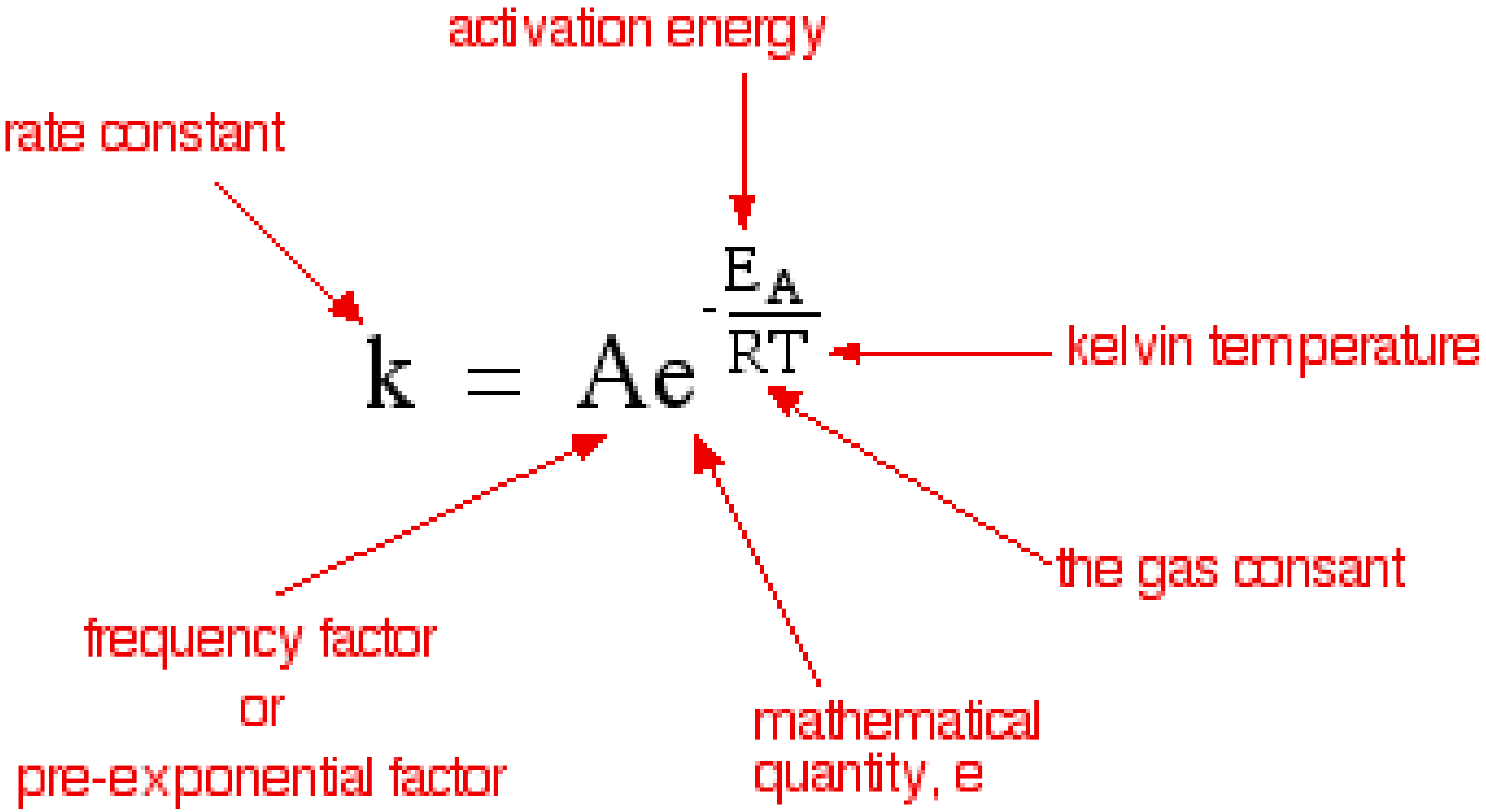
Arrhenius Relationship

- Relationship that is most commonly used in accelerated failure prediction
- Often used to model the effects of temperature
- ***Based on the assumption of a simple chemical reaction***
- Common application:

  Time to get to a set reduction in a physical property
- General rule of thumb is that every 10 °C rise in temperature results in doubling the rate of reaction
- Can be used to calculate the maximum service temperature

Arrhenius Relationship

Formula that is most commonly used in accelerated failure prediction



$$k = Ae^{-\frac{E_A}{RT}}$$

activation energy

rate constant

kelvin temperature

the gas consant

frequency factor
or
pre-exponential factor

mathematical
quantity, e

Arrhenius Relationship

Formula that is most commonly used in accelerated failure prediction

Temperature Coefficient (Q_{10})

Aging Factor

$$Q10 = (r2 / r1)^{10/(T2-T1)}$$

Rearranges to $AF = Q_{10}^{[(T2-T1)/10]}$

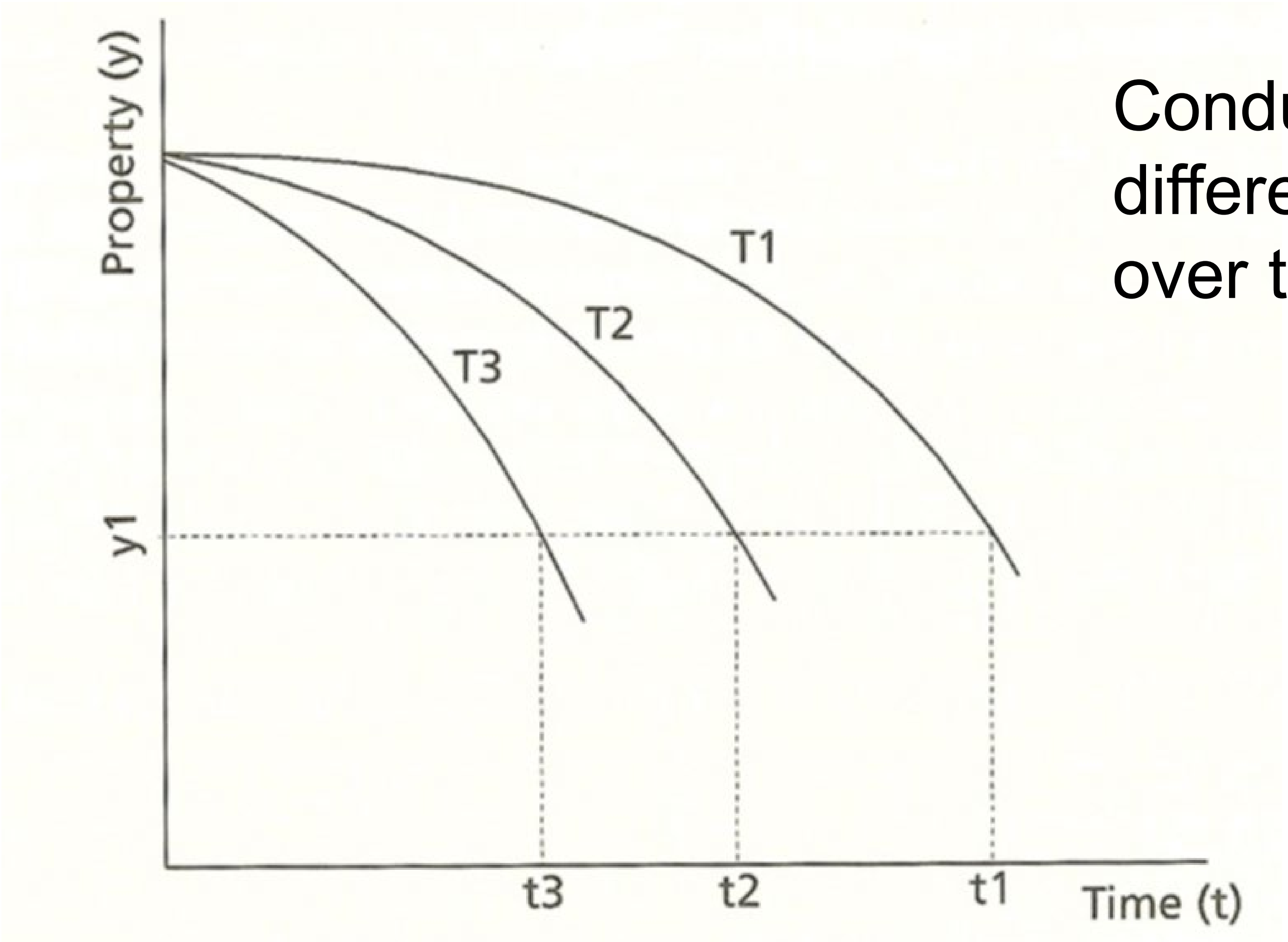
Q_{10} Is Typically Considered To Equal 2
Actual Experiments Show A Range of 1.8 to 2.5

Arrhenius Relationship

Formula that is most commonly used in accelerated failure prediction

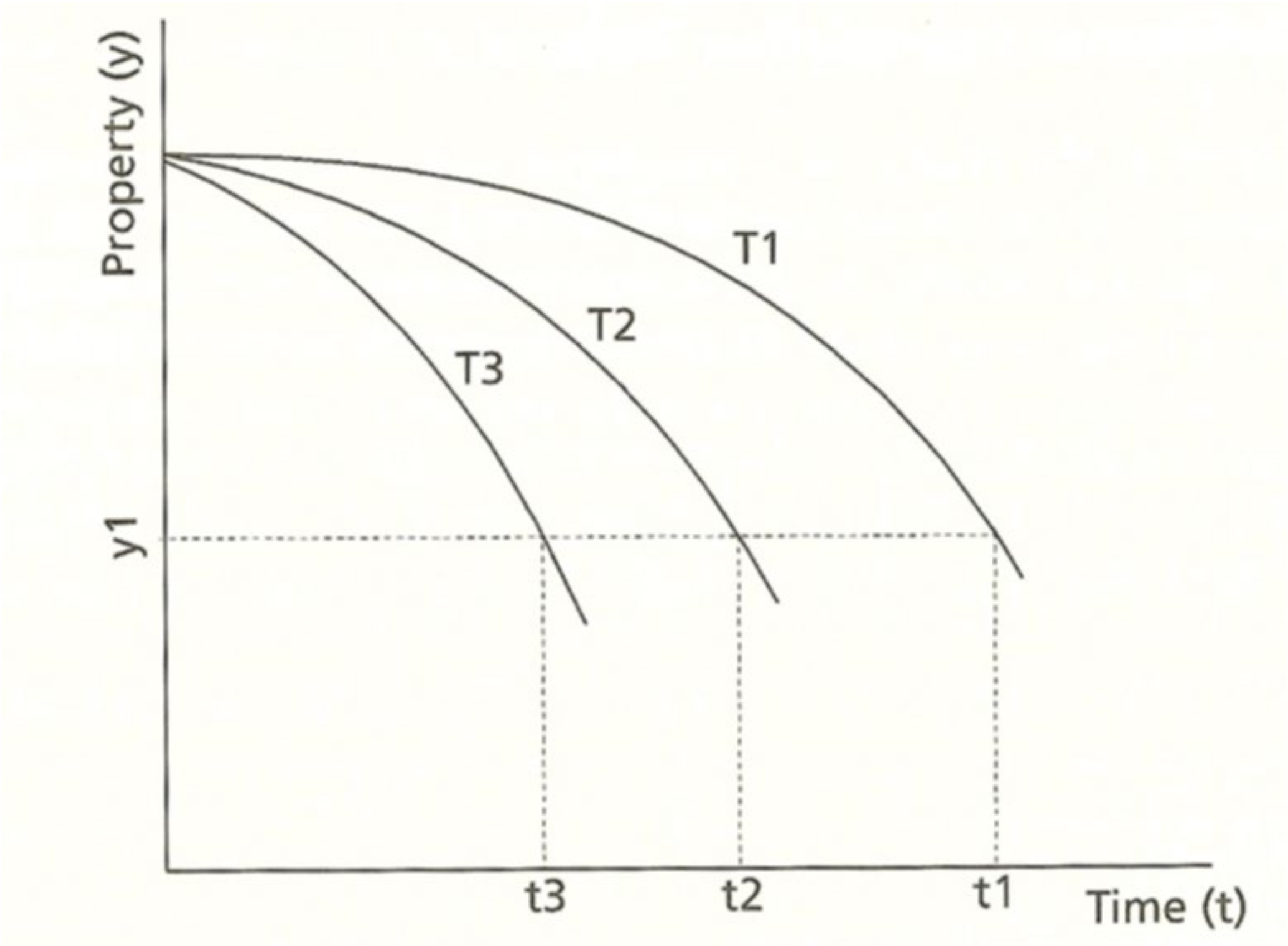
- Based on the assumption of a simple chemical reaction
- Increased temperature results in increased reaction rates
- Reaction rates are dependent on energy, collisions, temperature, and orientation

Arrhenius Experiment



Conduct a series of experiments at different temperatures – measure results over time

Arrhenius Experiment



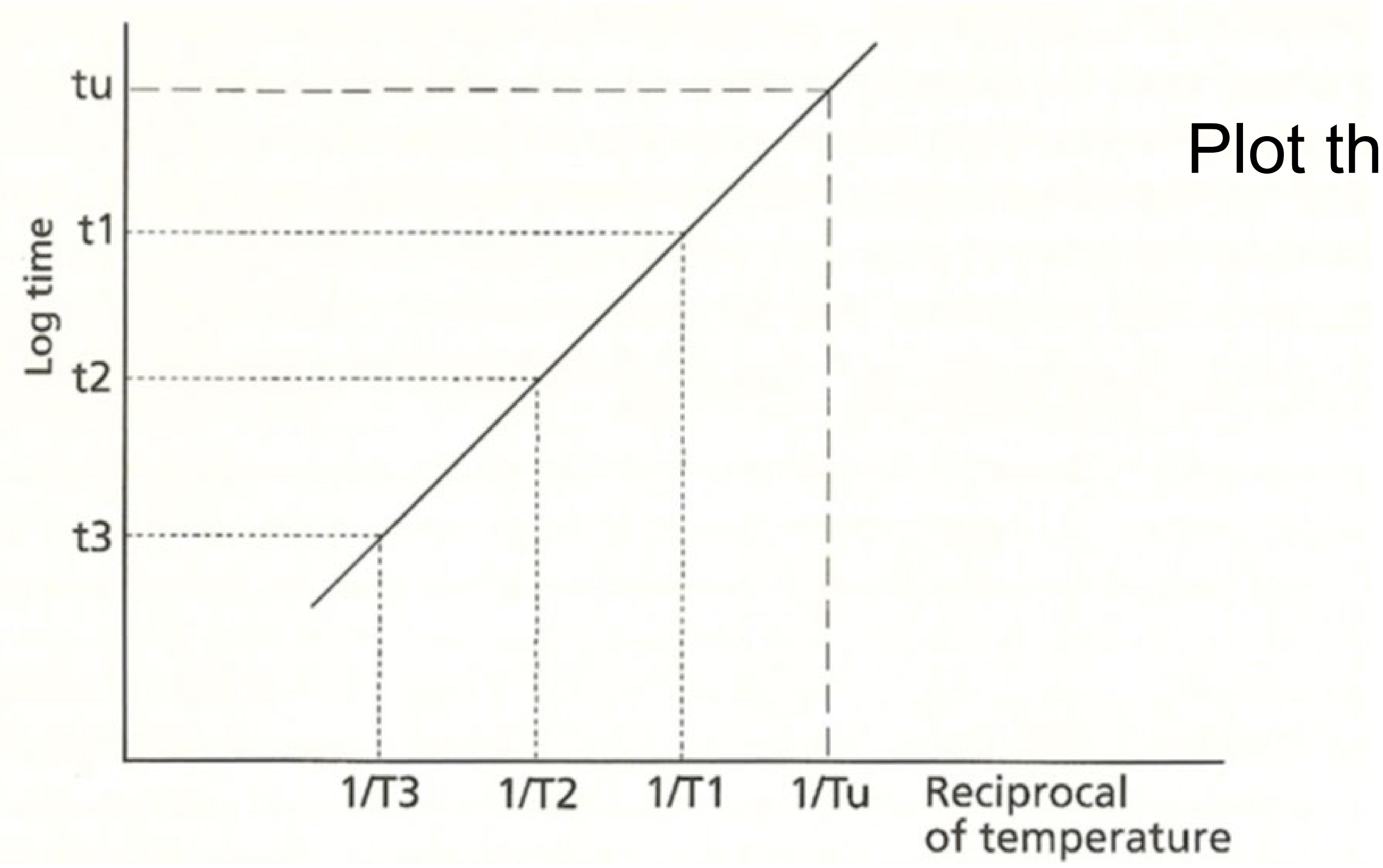
For example:
Place tensile bars in ovens at 3 different temperatures

- 50 °C
- 75 °C
- 90 °C

and test at 3 different times

- 100 hours
- 1000 hours
- 5000 hours

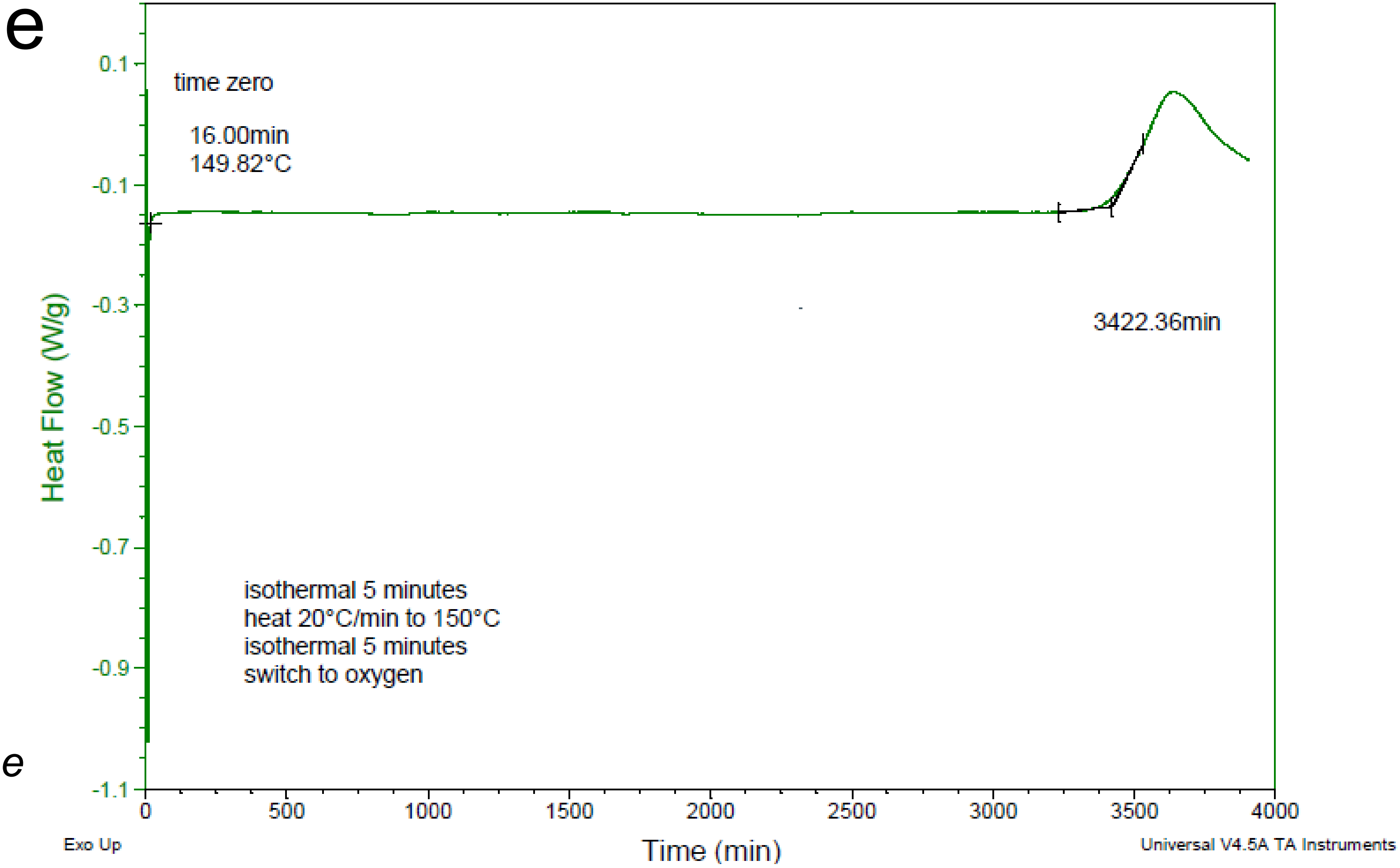
Arrhenius Experiment



Plot the results to create the model

Oxidative Induction Time Testing

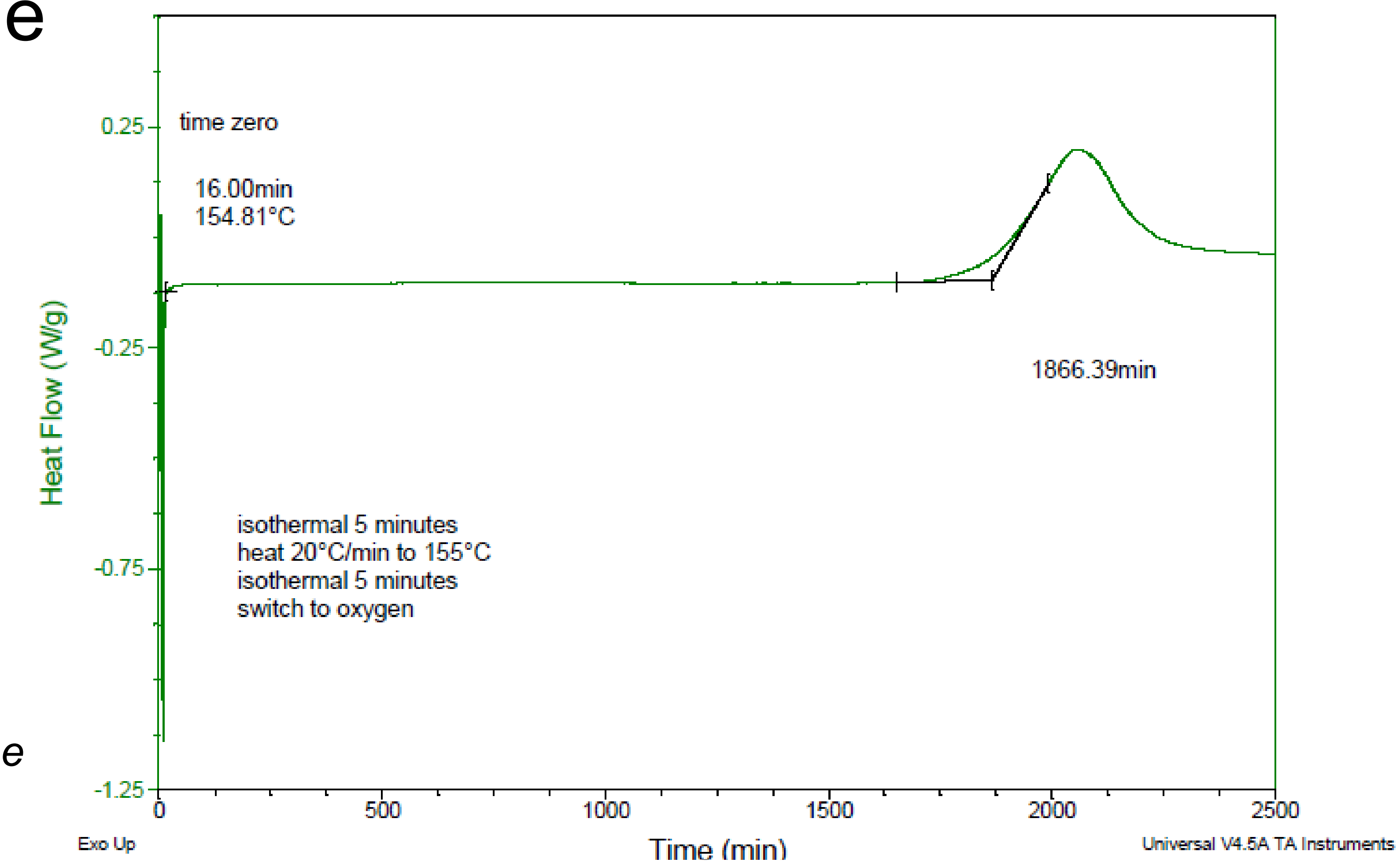
Oxidative Induction Time
Polypropylene, 150 °C



Data from Mike Sepe

Oxidative Induction Time Testing

Oxidative Induction Time
Polypropylene, 155 °C



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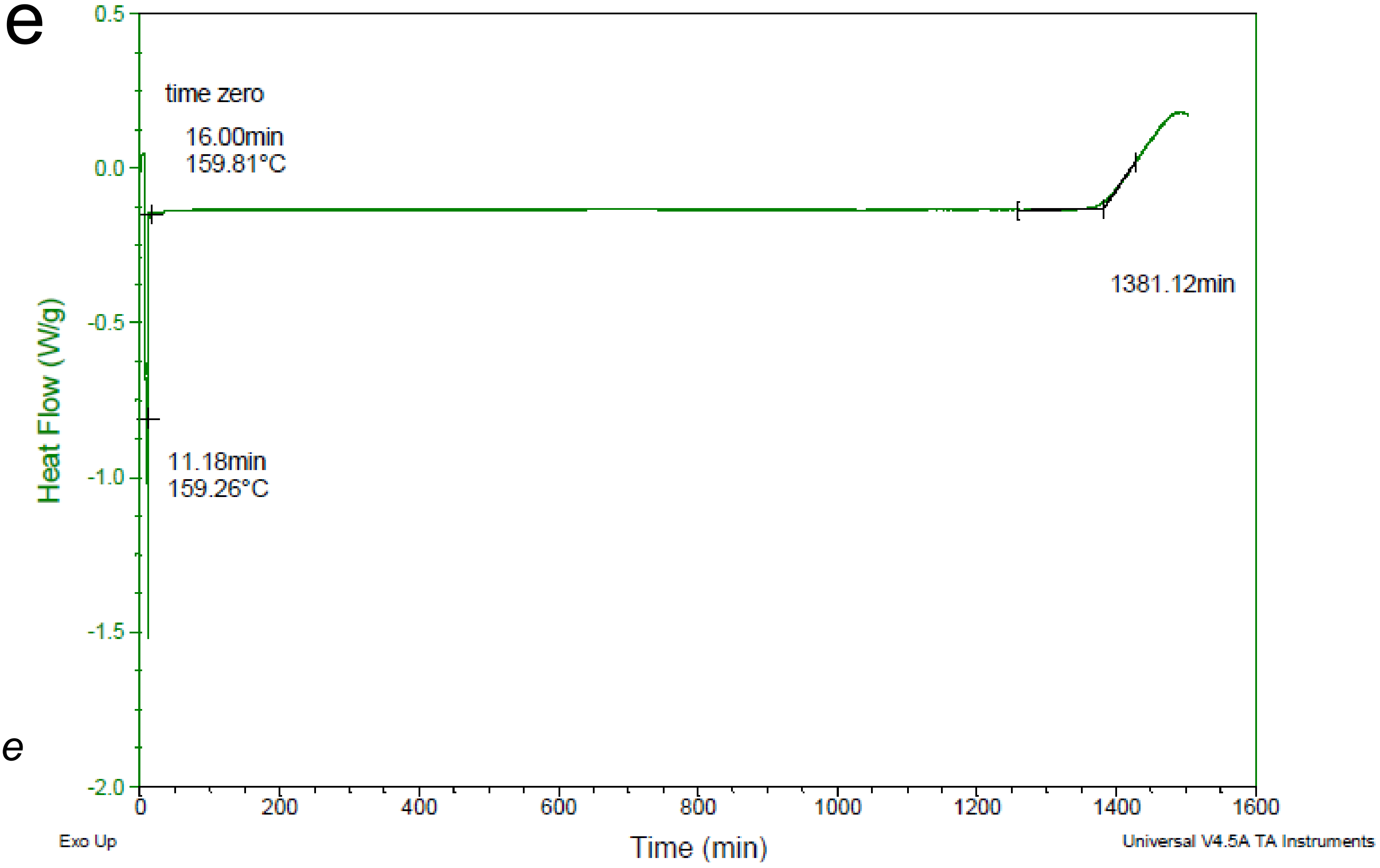
Oxidative Induction Time Testing

Oxidative Induction Time
Polypropylene, 160 °C



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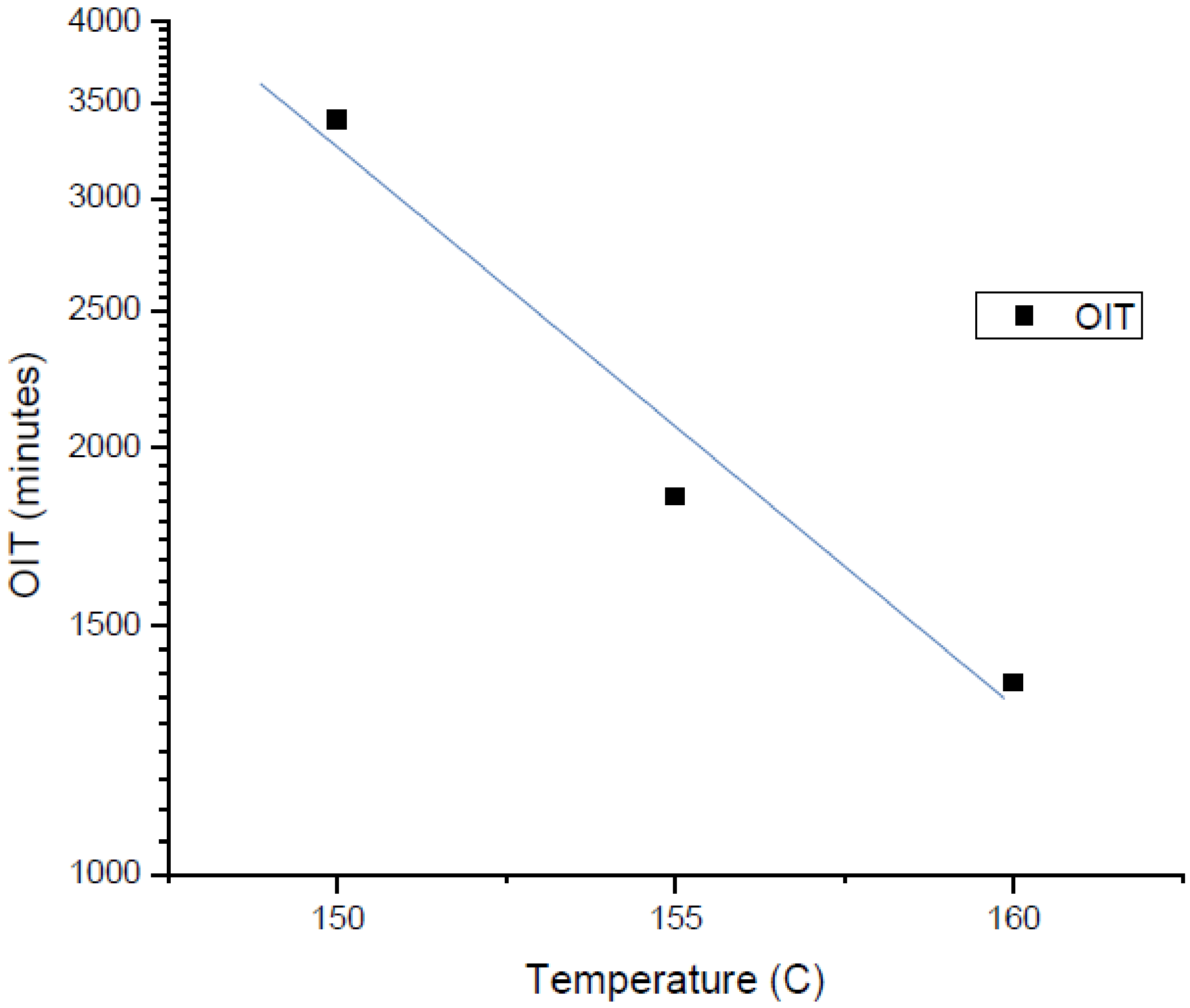
Oxidative Induction Time Testing

Plot of OIT versus Temperature for Three Tests



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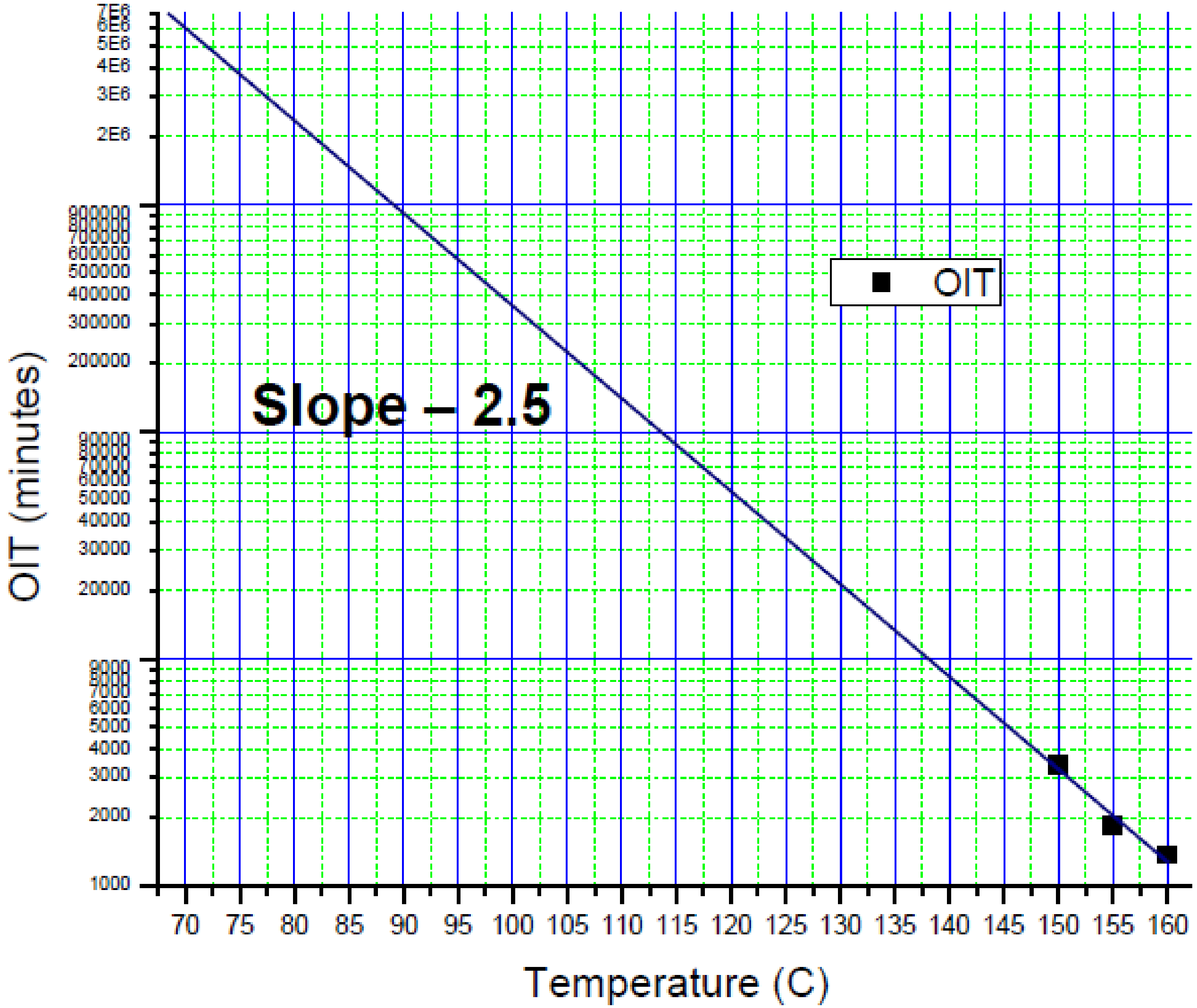
Oxidative Induction Time Testing

Plot of OIT versus Temperature Extrapolated



Data from Mike Sepe

Arrhenius Accelerated Aging Tests

Experimental Considerations

- Three to four experimental points should be used to confirm the aging factor
- Selected temperatures should not cross a key transition temperature
- Extrapolations should not extend across a key transition temperature
- Failure must be carefully refined (e.g. 50% reduction in a key property relative to initial performance)

Arrhenius Accelerated Aging Tests

The Problem:

Accelerated testing models assume that thermo-oxidation (a chemical reaction) is the ***ONLY*** mechanism in effect and ***ALL*** observed property changes are attributed to this mechanism

Arrhenius Accelerated Aging Tests

Considerations:

- Multiple processes frequently take place concurrently
- Some of these processes are thermally activated (require a specific minimum temperature to occur)
- Some are relaxation processes (will occur at some rate at any temperature)
- Approaching or exceeding key transition temperatures, such as Tg, may accelerate these processes to a much greater degree than predicted by traditional mathematical models

Alternate Mechanisms

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Alternate Mechanisms

Several “competing” mechanisms can take place during thermal aging tests

- Crystalline Structure Advancement / Reorganization

Crystalline Structure Advancement

- Exposure to temperatures above the glass transition temperature (Tg) can result in reorganization of the crystalline structure in semi-crystalline polymers
- Results in increased crystallinity
- Several semi-crystalline polymers Have Tg's Below 60 °C
  - Polyethylene
  - Polypropylene
  - Polyacetal
  - Polyketone
  - Conditioned Aliphatic Polyamides
- Does not follow the Arrhenius Relationship with temperature

Crystalline Structure Advancement

- Tensile strength increases by 8%
- Tensile modulus increases by 10%
- Ultimate elongation decreases by 55%
- *Tests of molecular weight and oxidative stability show no evidence of oxidative degradation*
- Property changes are consistent with crystallization

“Aging” Behavior in A Polypropylene

Property	Units	As Molded	Aged 60 Days @ 55^oC
Tensile Yield Strength	MPa	26.80	28.81
Tensile Modulus	MPa	1070	1176
Elongation @ Break	%	440	201

Data from Mike Sepe

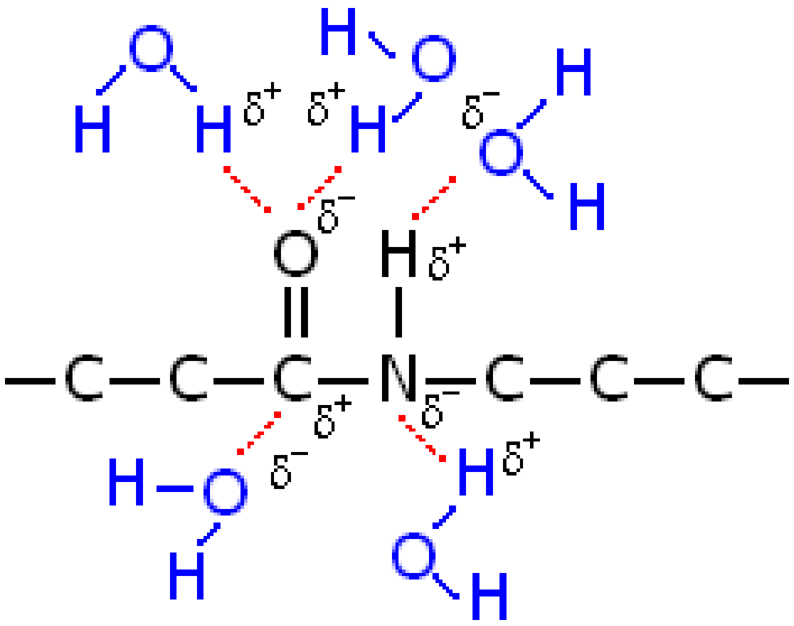
Alternate Mechanisms

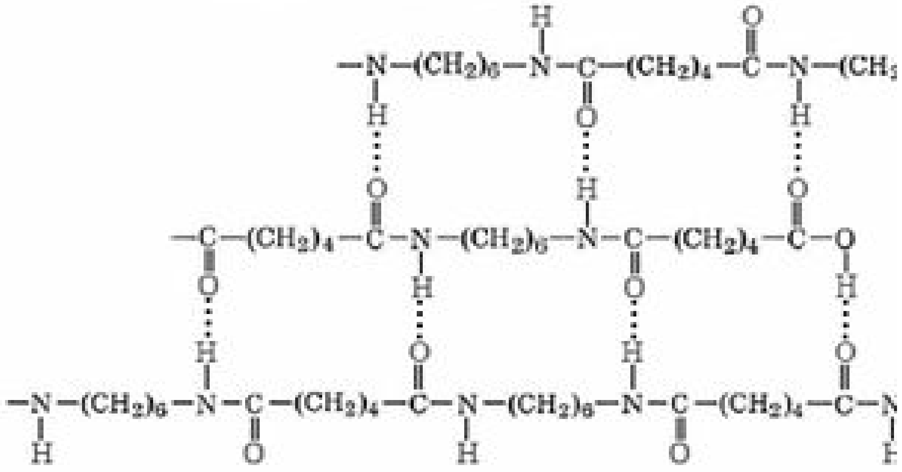
Several "competing" mechanisms can take place during thermal aging tests

- Crystalline Structure Advancement / Reorganization
- Moisture Conditioning of Nylon Resins

Conditioning of Nylon

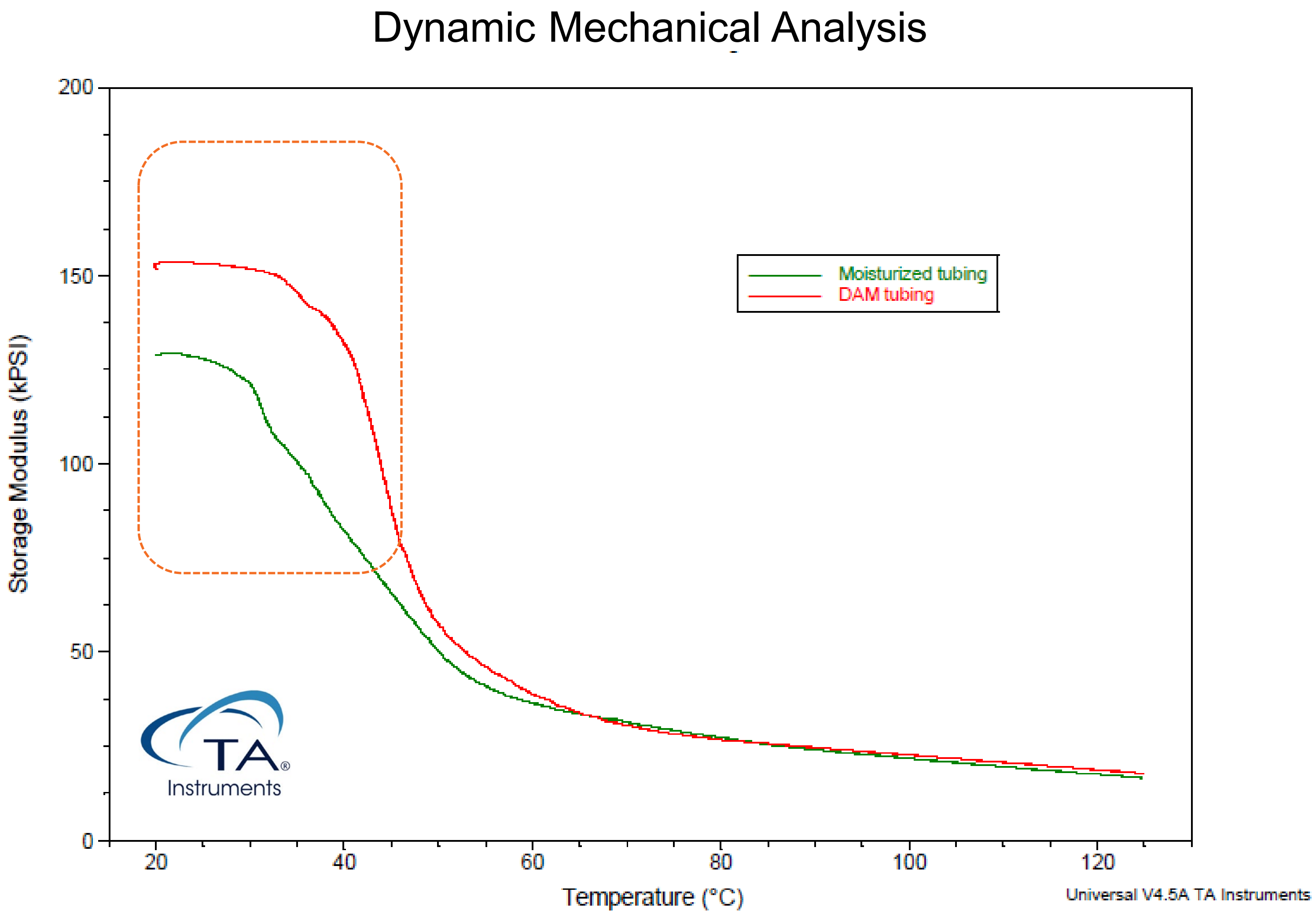
Absorption of water interferes with the intermolecular bonding between individual nylon polymer chains – results in changes in physical properties





Conditioning of Nylon

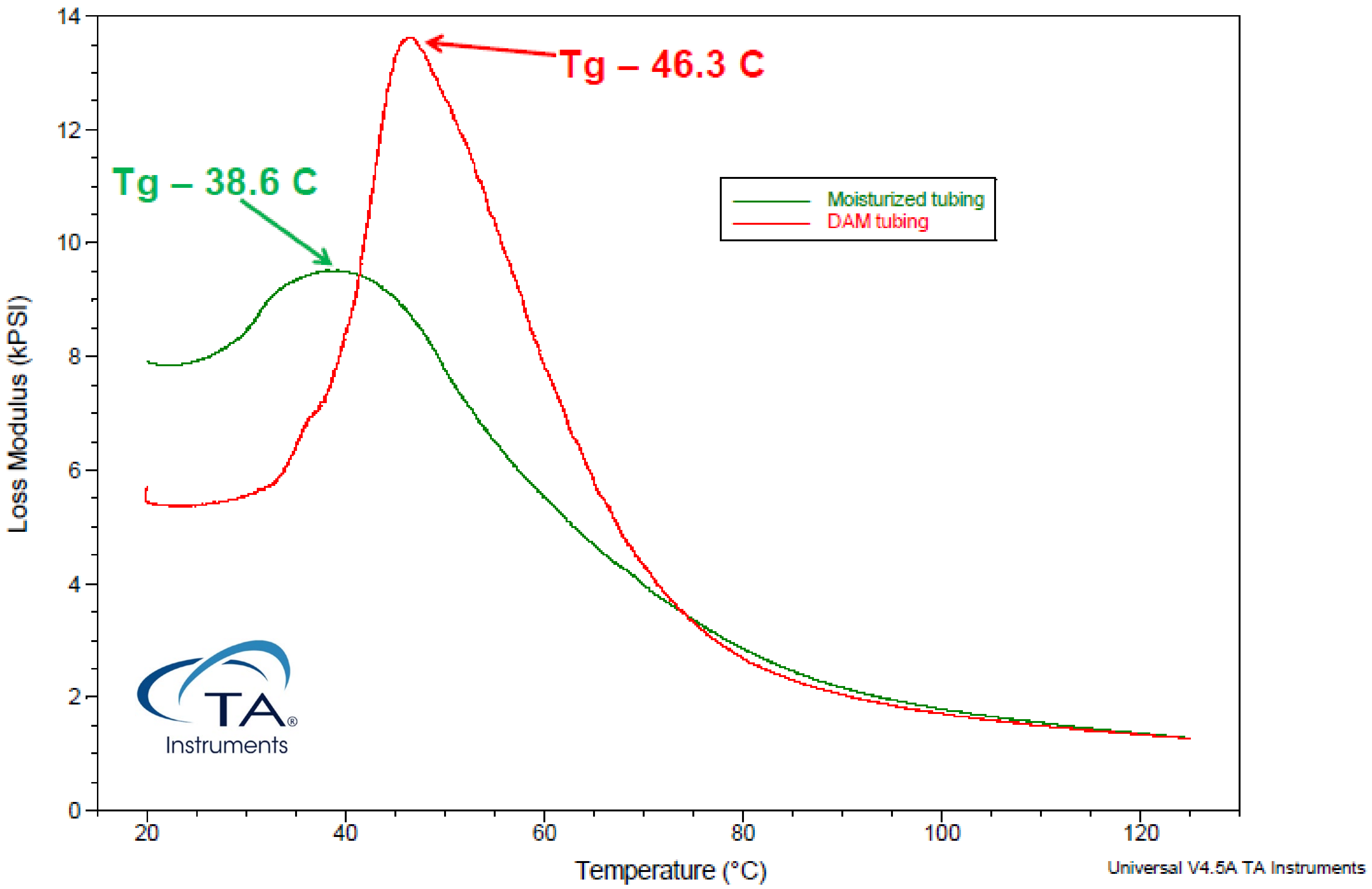
Effect of moisture absorption on Nylon 12 - Elastic modulus



Conditioning of Nylon

Effect of moisture absorption on Nylon 12 - Viscous modulus

Dynamic Mechanical Analysis



Alternate Mechanisms

Several "competing" mechanisms can take place during thermal aging tests

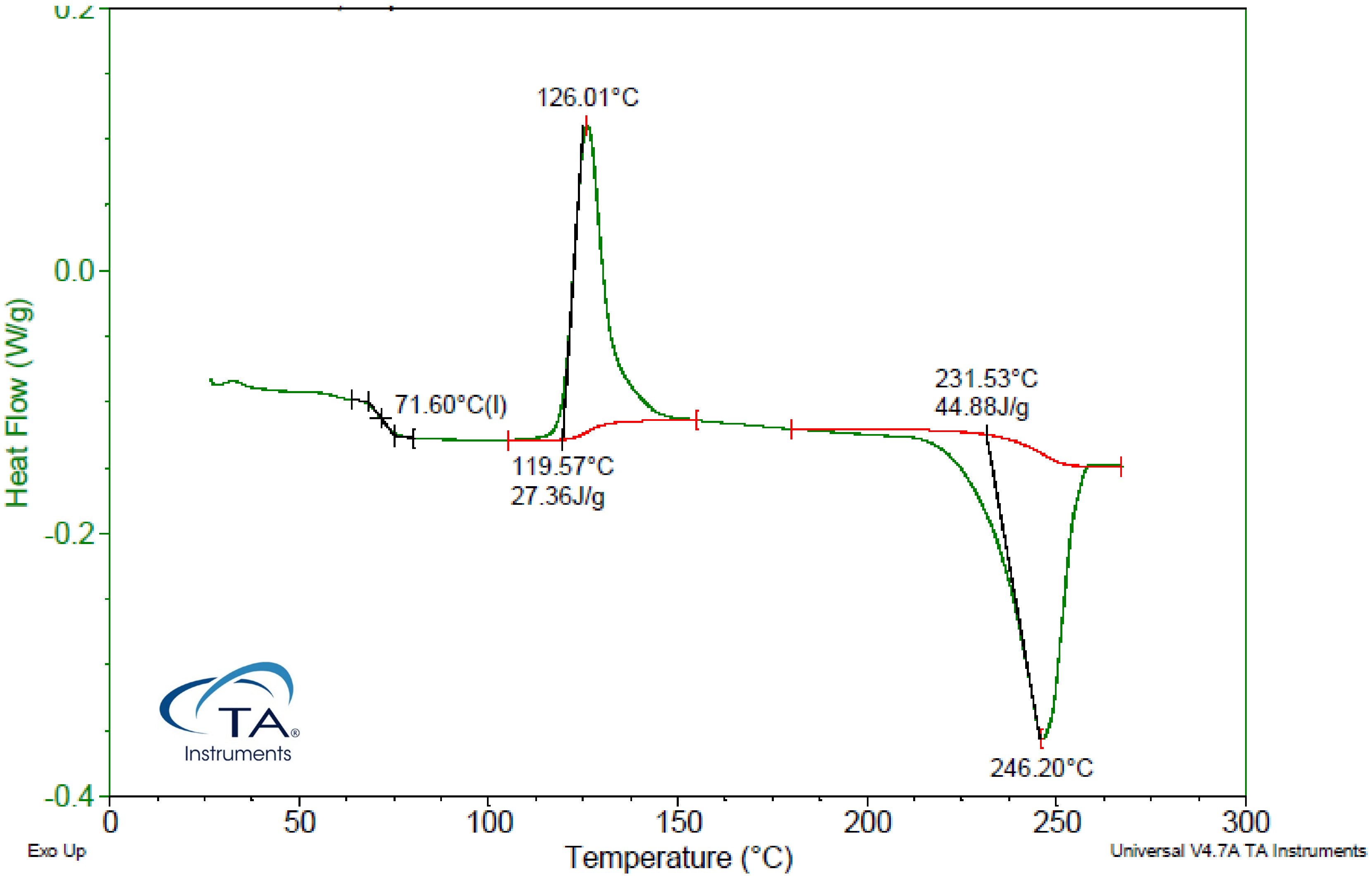
- Crystalline Structure Advancement / Reorganization
- Moisture Conditioning of Nylon Resins
- Physical Aging

Physical Aging

- Physical aging occurs in the amorphous regions of a polymer
- Process increases strength and modulus, but decreases ductility
- Occurs above the Beta transition of the polymer
- Occurs at a rate governed by the relationship between the aging temperature and the Tg
- Does not follow the Arrhenius Relationship with temperature
- Occurs more rapidly in low molecular weight systems

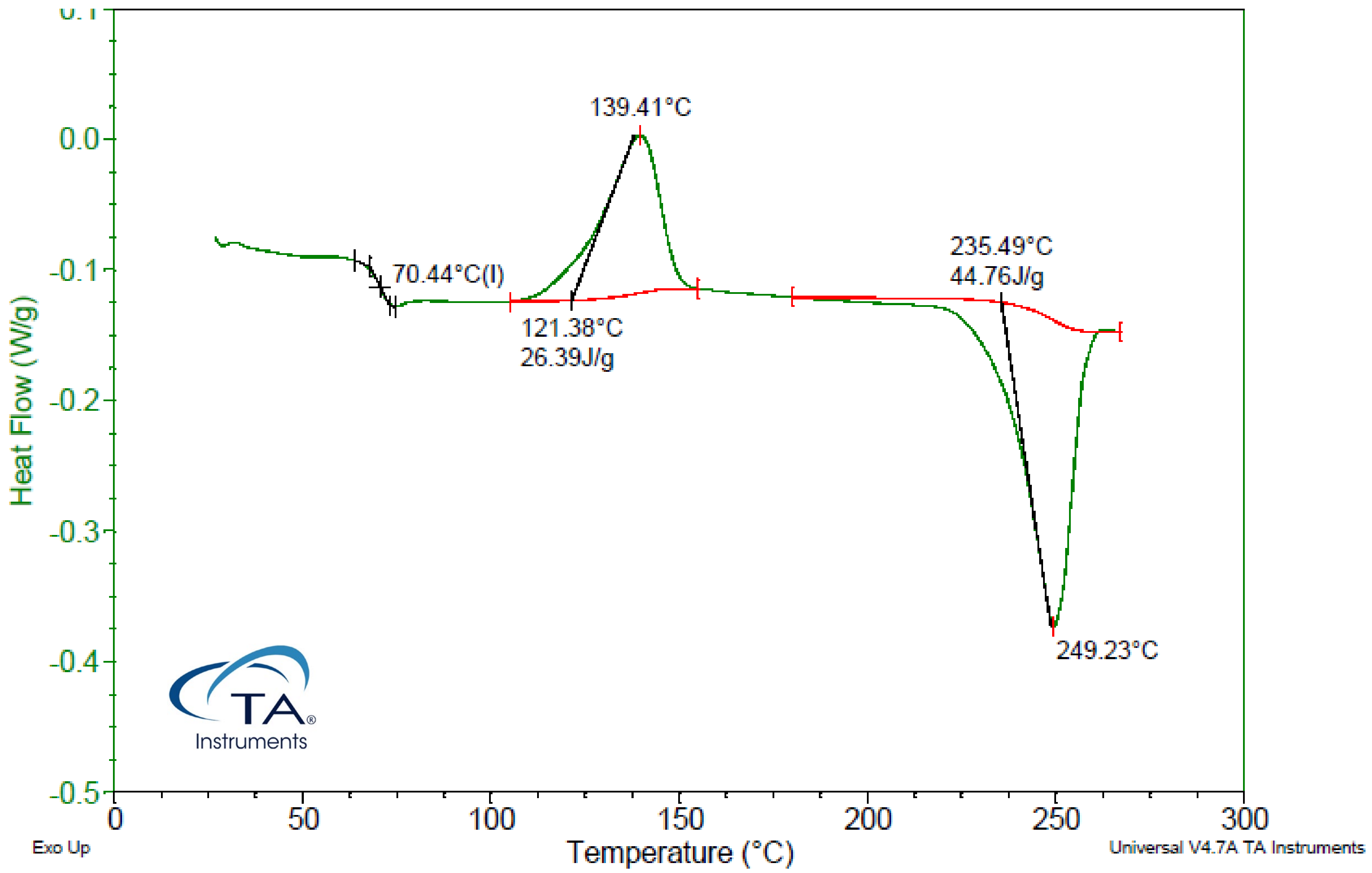
Physical Aging

DSC thermogram showing heat flow of an as-molded amorphous PET polyester



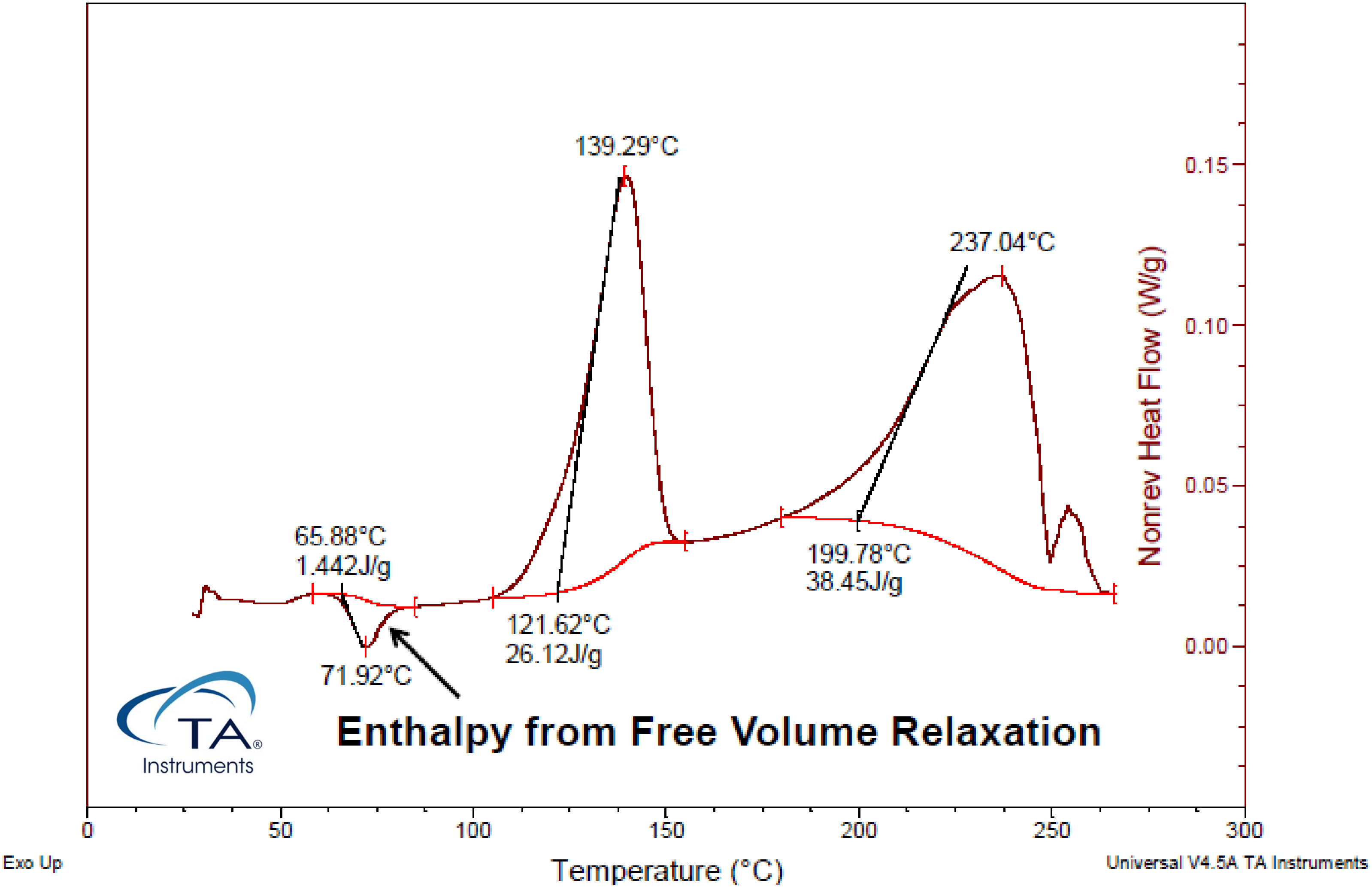
Physical Aging

DSC thermogram showing heat flow of amorphous PET polyester aged at 50 C for 18.75 hours



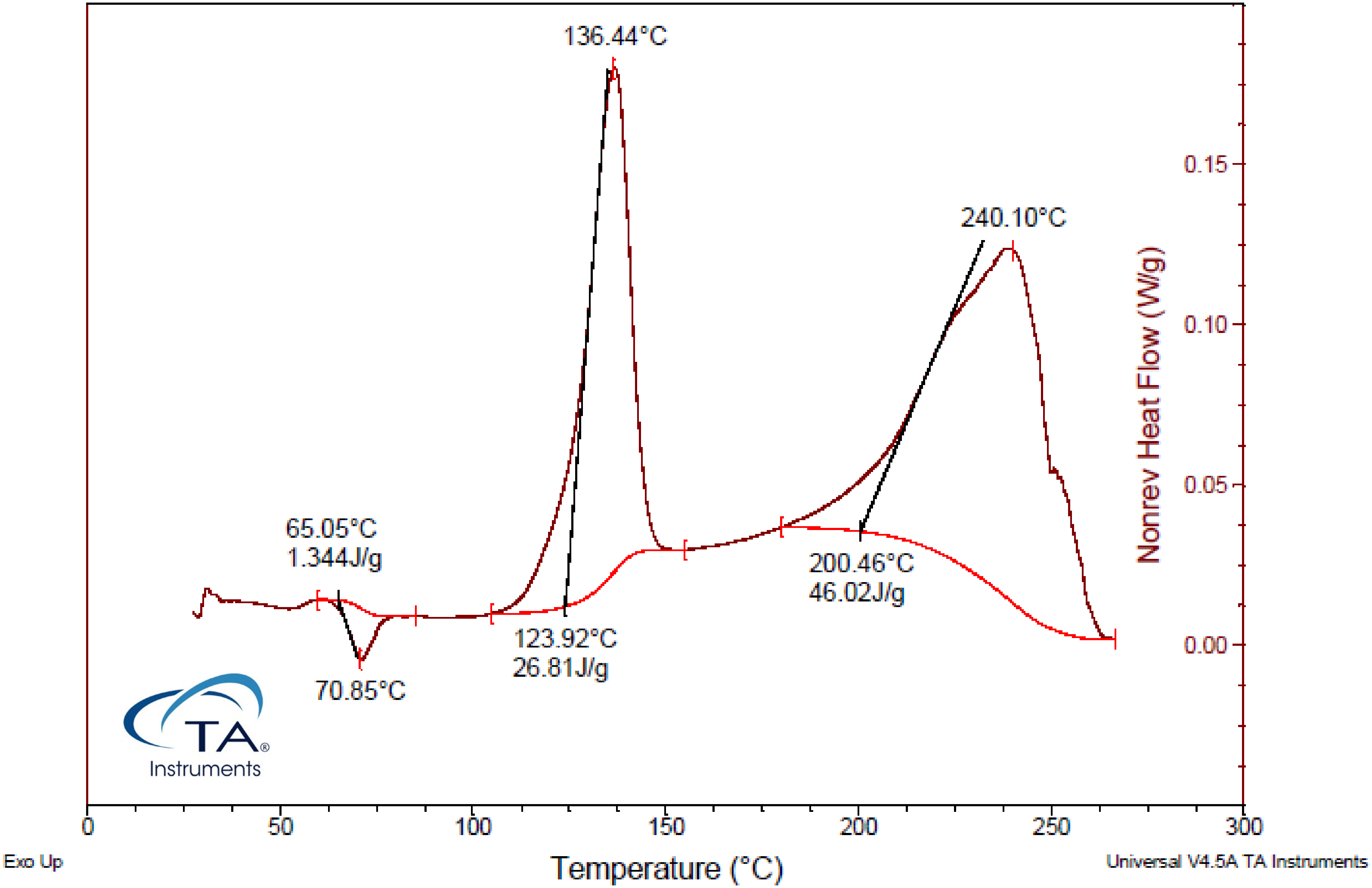
Physical Aging

DSC thermogram showing heat flow of amorphous PET polyester aged at 50 C for 18.75 hours



Physical Aging

DSC thermogram showing heat flow of amorphous PET polyester aged at 20 C for 25 months



Physical Aging

Acceleration factor for physical aging in amorphous PET

- 18.75 hours at 50 C is equivalent to 18000 Hours at 20 C
- Q10 = 9.91
- Studies conducted at Eastman obtained a result of 9.8 using more extensive data
- Physical aging is the dominant mechanism when compared to oxidation

Alternate Mechanisms

Several "competing" mechanisms can take place during thermal aging tests

- Crystalline Structure Advancement / Reorganization
- Moisture Conditioning of Nylon Resins
- Physical Aging
- Creep

Creep

Creep is…..

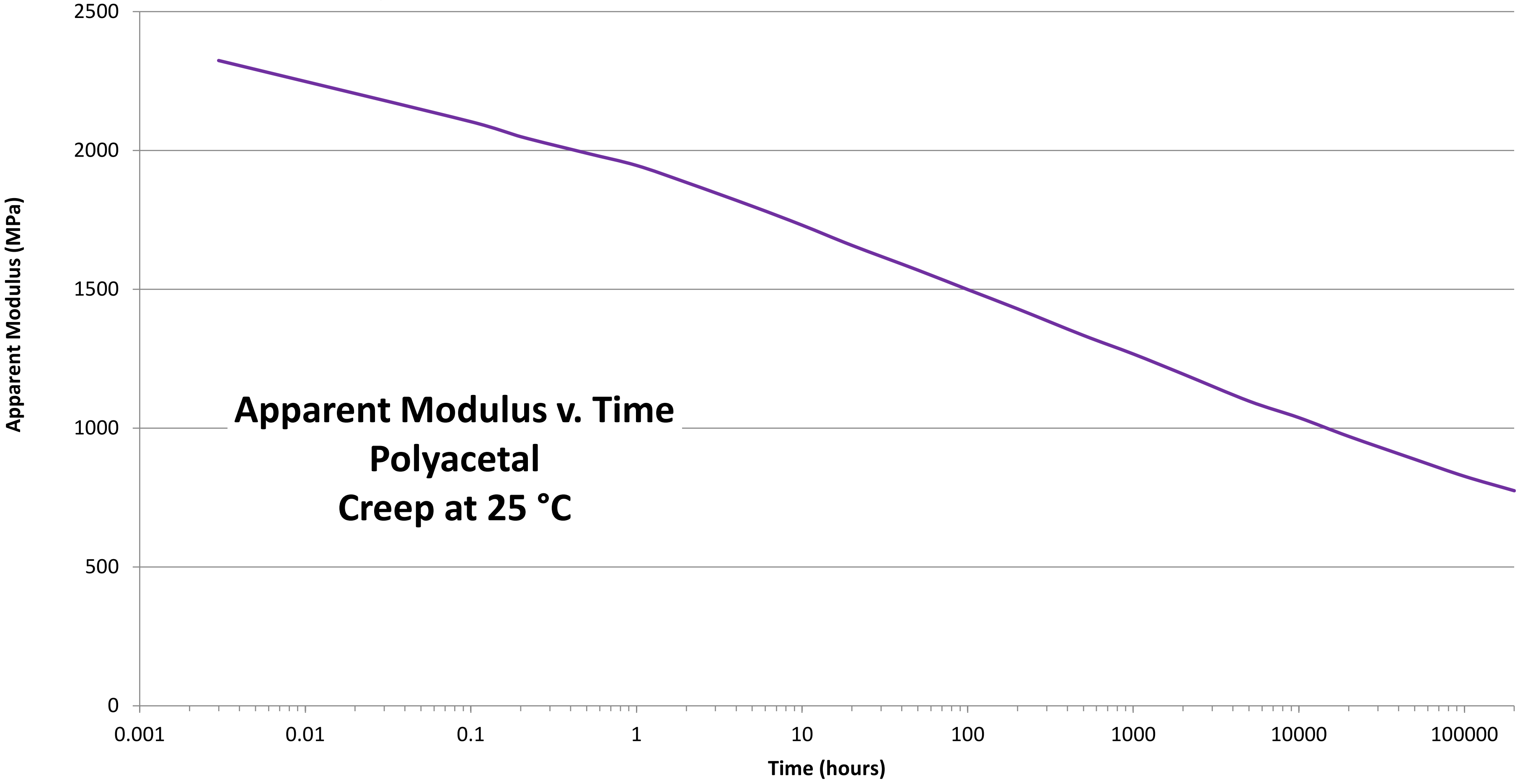
the tendency of a solid material to deform permanently under the influence of constant stress (tensile, compressive, shear, or flexural). It occurs as a function of time through extended exposure to levels of stress that are below the yield strength of the material.

Creep

- Low to moderate forces exerted over an extended time → lower ductility. Can result in brittle fracture in normally ductile plastics
- Inherent viscoelastic nature of polymers leads to time dependency
- Prolonged static stresses lead to a decay in apparent modulus through localized molecular reorganization of polymer chains
- At stresses below the yield point molecular reorganization includes disentanglement as there is no opportunity for yielding
- Accelerated by temperature - does not follow the Arrhenius Relationship with temperature

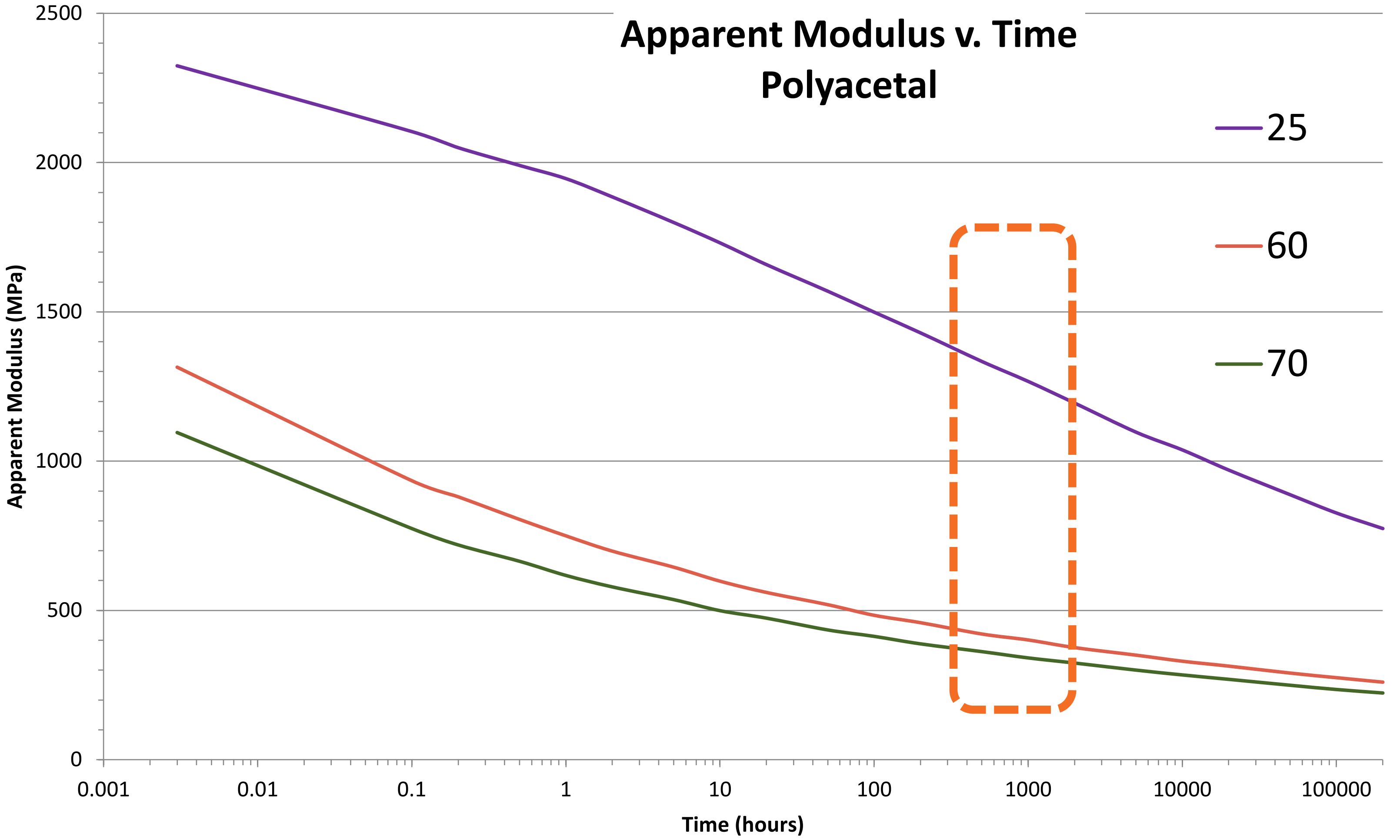
Creep Projection

Creep master curve as semi-log plot



Creep Projection

Creep master curve as semi-log plot



Realtive Theraml Index

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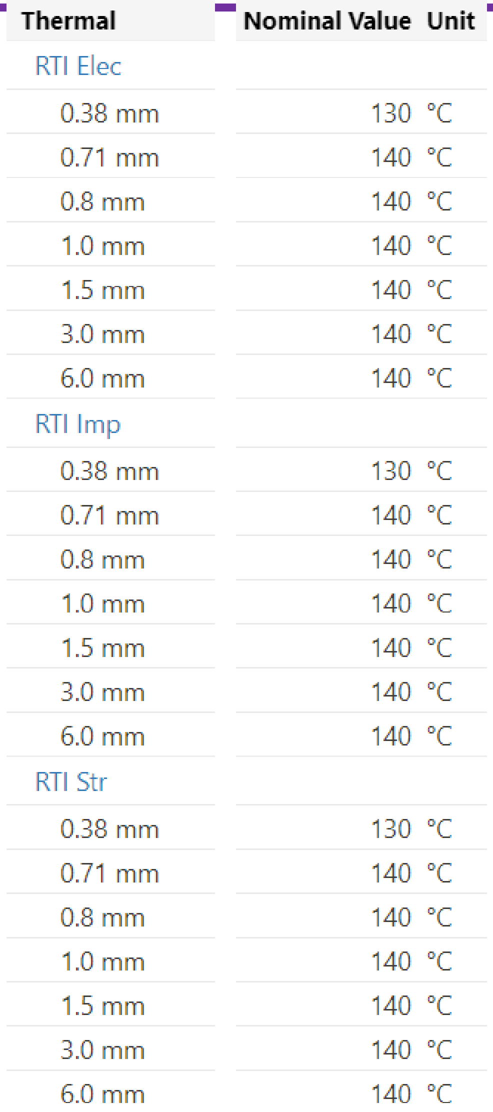
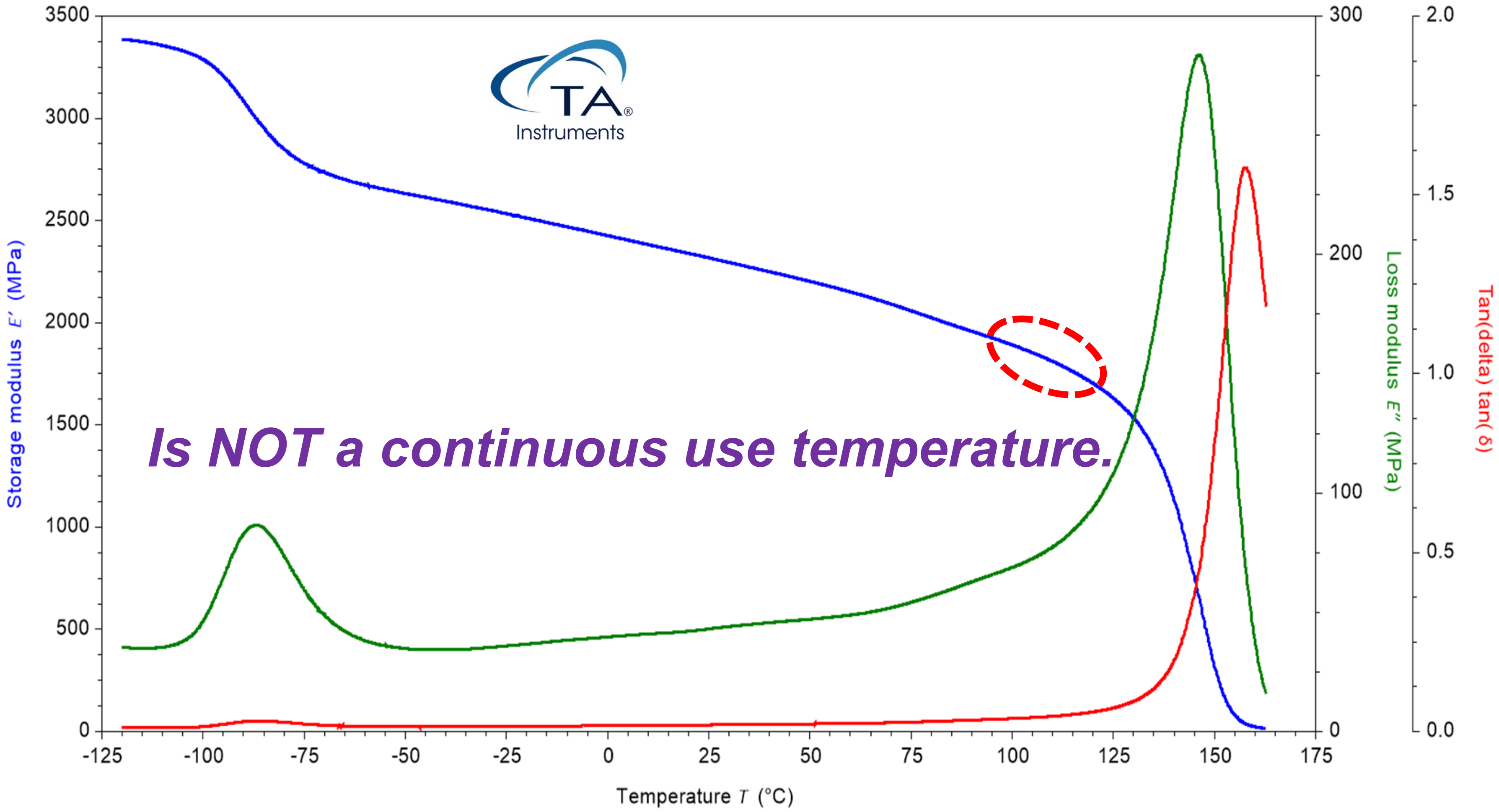
Relative Temperature Index

- The Relative temperature index (RTI) is a characteristic parameter related to the thermal degradation of plastics.
- Measured as part of UL746B.
- Evaluates Strength, Impact, and Electrical properties.
- The RTI is the temperature (°C) in at which the properties have decreased to 50 percent of their initial value after a long-term exposure to this temperature.



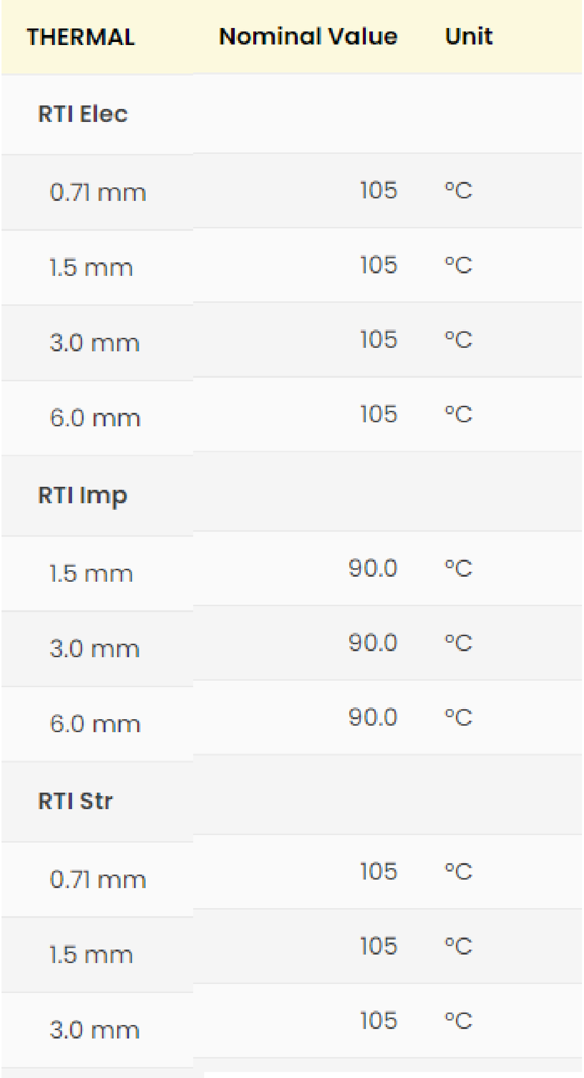
Thermal	Nominal Value	Unit
RTI Elec		
0.38 mm	130	°C
0.71 mm	140	°C
0.8 mm	140	°C
1.0 mm	140	°C
1.5 mm	140	°C
3.0 mm	140	°C
6.0 mm	140	°C
RTI Imp		
0.38 mm	130	°C
0.71 mm	140	°C
0.8 mm	140	°C
1.0 mm	140	°C
1.5 mm	140	°C
3.0 mm	140	°C
6.0 mm	140	°C
RTI Str		
0.38 mm	130	°C
0.71 mm	140	°C
0.8 mm	140	°C
1.0 mm	140	°C
1.5 mm	140	°C
3.0 mm	140	°C
6.0 mm	140	°C

Relative Temperature Index



Dynamic Mechanical Analysis

Is NOT a continuous use temperature.



THERMAL	Nominal Value	Unit
RTI Elec		
0.71 mm	105	°C
1.5 mm	105	°C
3.0 mm	105	°C
6.0 mm	105	°C
RTI Imp		
1.5 mm	90.0	°C
3.0 mm	90.0	°C
6.0 mm	90.0	°C
RTI Str		
0.71 mm	105	°C
1.5 mm	105	°C
3.0 mm	105	°C

Conclusions

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Conclusions

- Elevated temperatures used in accelerated aging tests can promote multiple mechanisms
  - Thermo-oxidation
  - Crystallinity restructuring
  - Moisture conditioning
  - Physical aging
  - Creep
- Accelerated aging protocols tend to ascribe all the observed property changes to thermo-oxidation
- Frequently another mechanism is dominant

Conclusions

- Several different aging effects can be factors simultaneously
- Failure to recognize these other mechanisms and identify the most important one can result in flawed test plans and conclusions
- Often these factors follow different acceleration rates
  - Mechanisms can be accelerated by temperature great than predicted by Arrhenius
  - Mechanisms can occur in real time testing that do not have time to take place in accelerated protocols

Thank you!

THE
MADISON GROUP
PLASTIC CONSULTING ENGINEERS

The Madison Group is the recognized leader in plastics engineering. Over the course of three decades The Madison Group has focused on polymeric materials. We understand how these materials behave, how to properly design with them, how they are processed, and the numerous manufacturing steps required to produce a successful product. Our capabilities include:

- Design Review
- Material Support
- Product Testing
- Manufacturing Support
- Failure Analysis
- Customized Training

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Thank you – Questions?

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